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Several widely employed test methods for the iodimetric measurement of hydrogen sulfide in refinery fuel gases are shown to suffer from serious thiol interferences. An absorbing solution consisting of 0.16 M cadmium sulfate/sulfuric acid at pH 3.0, is shown to be effective for the collection of hydrogen sulfide in the 70-700 mg/m^3 range and to be essentially free from interference by up to 1800 mg/m^3 of methanethiol. When combined with a single 3 percent hydrogen peroxide impinger, sulfur dioxide interferences of up to 1,300 mg/m^3 are also removed. No measureable interference results from the presence of carbon oxysulfide, ethene, dimethyl sulfoxide, or thiophene. Acetaldehyde and acetone are observed to interfere at the 2,400 and 48,000 mg/m^3 level, respectively. It is proposed that the absorption solution described here be substituted for the cadmium hydroxide/cadmium sulfate mixture used in the EPA test method (Method 11) for determining the hydrogen sulfide content of refinery fuel gases.

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DETERMINATION OF HYDROGEN SULFIDE IN REFINERY FUEL GASES

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DISCLAIMER

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ABSTRACT

EPA Test Method 11 has been evaluated. In this study, the cadmium hydroxide/cadmium sulfate gas absorbing solution was found to be an efficient collector of thiols. Since thiols are iodimetrically active and often found present together with hydrogen sulfide in refinery fuel gases, they cause a serious interference in the method. The same problem was found to exist when several other gas absorbing solutions were studied. These included neutral cadmium sulfate, neutral zinc acetate, as well as buffered cadmium acetate, cadmium formate and zinc acetate solutions. Large interferences occurred when thiols were simultaneously present with hydrogen sulfide and coprecipitation took place. Further investigation produced an absorbing solution that is essentially free from thiol interference. This has been achieved using 0.16M $CdSO_4$ solution, adjusted to pH 3.9 with H_2SO_4, which is effective for the collection of H_2S in the 23-700 mg/m^3 range, in the presence of up to 1800 mg/m^3 of CH_3SH.

Sulfur dioxide in the 1300 mg/m^3 range was found to be effectively removed by the single midget impinger of 3 percent H_2O_2 specified in Method 11. Less than 0.2% of the H_2S was removed by this reagent and interferences resulting from its evaporative entrainment were negligible. The peroxide solution also was shown to serve as a physical trap for other unwanted substances.

Compatibility of the absorbing solutions under study with iodimetric measurement was shown and cadmium sulfide precipitates aged for ten days did not differ from freshly prepared samples when analyzed.

Further studies were also made employing other substances often present in refinery fuel gases. No measurable interference resulted from the presence of carbon oxysulfide, dimethyl sulfoxide, ethene or thiophene. Acetaldehyde and acetone were observed to interfere at the 24000 and 48000 mg/m^3 level, respectively. The former substance was largely removed by the air flush procedure and the latter substance was trapped, to a large extent, in the peroxide solution.

A revised version of the test method is presented.

This report covers a period from January 1, 1974 to December 31, 1975 and work was accomplished as of December 31, 1975.

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SECTION 1

INTRODUCTION

In view of the increasing national concern about toxic sulfur compounds in the atmosphere, the U.S. Environmental Protection Agency (EPA) has issued regulations that deal with the emission of sulfur dioxide into the atmosphere from the combustion of petroleum refinery fuel gases and process gases that contain hydrogen sulfide. In March 1974, a standard was promulgated that limited the emission of sulfur gases from fuel gas combustion devices by specifying that the fuel gas combusted contain no more than 230 mg/dscm of H_2S, or optionally, that the gases resulting from the combustion of fuel gas be treated in a manner which limits the release of SO_2 into the atmosphere.[1] The applicable performance test method for H_2S, designated EPA Method 11,[2] utilizes an alkaline $CdSO_4$ solution to collect H_2S, which is later regenerated and measured iodimetrically. Other methods have also been developed for the analysis of gases containing H_2S, and recently the literature has been reviewed.[3] Two iodimetric procedures that have also been widely employed are the "ASTM Method D2385-66-T,"[4] which uses $CdSO_4$ and a method which uses $Zn(C_2H_3O_2)_2$.[5]

In recognition of the acute need for accurate techniques, EPA's Environmental Monitoring and Support Laboratory (EMSL) has been given the task of evaluating the standardizing test procedures in current use. This task has included the investigation of interferences in Method 11. Iodometry is not specific for H_2S; other substances that are often found present in refinery gases are also iodimetrically active. Among these, for example is SO_2 and Method 11 includes a H_2O_2 solution for the removal of SO_2 from the gas under analysis, prior to its passage through the H_2S absorption solution.

Recent attention to the fact that thiols may also be important constituents of refinery fuel gases, prompted the present study which is mainly concerned with the elimination of interferences resulting from these substances. To this end, collection efficiences of H_2S and CH_3SH were measured in several reagents, and the effects of varying concentration and pH were determined. Serious levels of interferences were found in all three of the methods cited above,[3,4,5] but a useful H_2S absorbing medium was developed. Some information was also obtained on the efficacy of removal of SO_2 by the H_2O_2 absorbing solution. And further, since entrained H_2O_2 may itself interfere in subsequent analytical processes, a study was also made of the minimum quantity transported as a result of evaporation and its fate in the H_2S absorbing solution. Interferences resulting from several other substances commonly found in fuel gases were also briefly considered. These data are presented below.

SECTION 2

CONCLUSIONS

This investigation has produced an absorbing solution that is essentially free from thiol interferences for use in the measurement of H_2S in refinery gases. This has been achieved using 0.16 M $CdSO_4$ solution adjusted to pH 3.0 with H_2SO_4, which is effective for the collection of H_2S in the 70-700 mg/m^3 range, in the presence of up to 1,000 mg/m^3 of CH_3SH. Recommendation of this solution as a substitute for the collecting medium now employed in EPA Method 11 is planned. (A revised version of the method is contained in Appendix A of this report.)

Serious thiol interferences were uncovered when neutral cadmium sulfate[5], alkaline cadmium sulfate (current EPA Method 11),[2] neutral zinc acetate[3] as well as when buffered cadmium acetate, cadmium formate and zinc acetate solutions were used.

Sulfur dioxide in the 1,300 mg/m^3 range is effectively removed by a single impinger of 3 percent H_2O_2. Interferences caused by the evaporative entrainment of the latter compound are negligible.

No measurable interference resulted from the presence of carbon oxysulfide, ethene, dimethyl sulfoxide, or thiophene. Acetaldehyde and acetone were observed to interfere at the 2,400 and 48,000 mg/m^3 level, respectively.

Equations pertaining to the relevant chemical processes are tabulated in Appendix B.

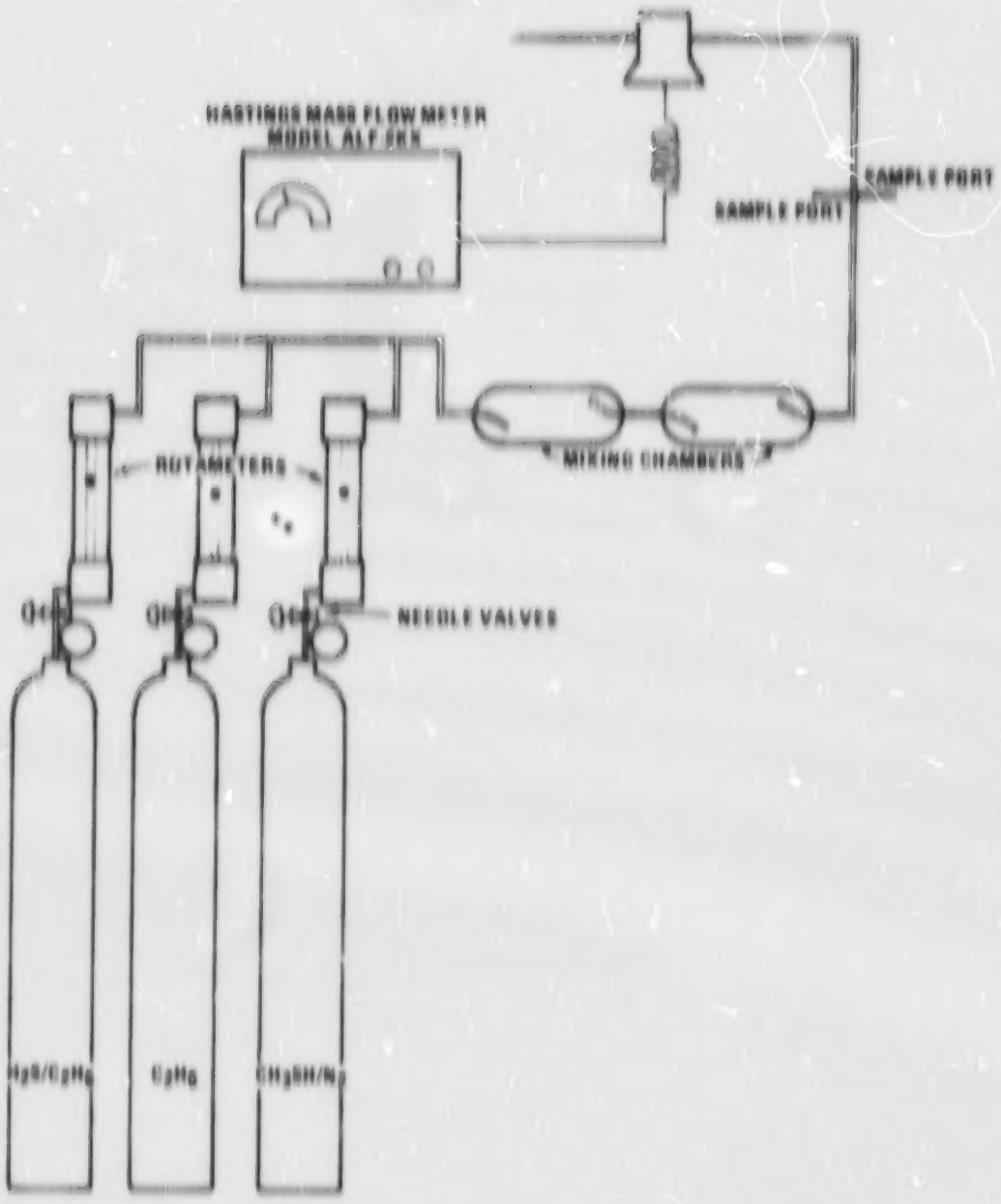

Figure 1. H_2S absorption flow apparatus.

SECTION 3

EXPERIMENTAL

Since refinery fuel gases consist of mixtures of light hydrocarbons which cannot easily be duplicated in the laboratory, C_2H_6 was selected as a diluent to prepare feed gases containing the sulfur compounds of interest. Hydrogen sulfide/ethane, methanethiol/nitrogen, sulfur dioxide/ethene mixed gases and ethane gas for further dilution obtained from a commercial supplier, were employed. The gas cylinders used were connected to the laboratory gas dilution system (shown in Figure 1) by means of 1/4" I.D. stainless steel tubing and joined with stainless steel Swagelock connectors. In each case, the gas passed through a Hoke type 1315g4Y metering valve and into a Dwyer 1 to 9 l/min rotometer-type flow meter. The three gas inputs connected into the manifold through a T-joint and the combined gases passed through two, 200 ml mixing chambers. A second T-joint afforded symmetrical sampling ports to which the sampling trains could be connected and duplicate samples withdrawn. The system was operated slightly above atmospheric pressure and exhausted through a Hastings Model ALF-25z Flow Meter, which was used to monitor flow and compute dilution factors. The sampling trains are described in Appendix A.

Cadmium sulfate/cadmium hydroxide, cadmium acetate, cadmium formate, cadmium sulfate/sulfuric acid and zinc acetate absorbing solutions were prepared from analytical grade reagents. Buffered absorbing solutions were prepared by mixing appropriate quantities of salt and acid and determining pH with a pH meter. Collection efficiencies of H_2S and CH_3SH were measured in these solutions over a range of pH values, employing gas streams containing diluted H_2S and CH_3SH (separately) and mixtures of H_2S and CH_3SH.

The gas sampling and analytical procedures described in Method 11[2] were followed, except as noted below. In practice, feed gas passed through a midget bubbler containing 15 ml of 3 percent H_2O_2 solution and then through three midget impingers, each containing 15 ml of the absorbing solution under investigation. The gas was collected for 10 minutes at a flow rate of approximately one l/min, which was followed by a 15 minute air flush at the same flow rate. This is typical of the procedure followed in practical stack sampling. Impingers containing the absorbed sulfur compounds were extracted with acid-iodine solution and analyzed iodimetrically. An identical impinger extraction procedure was followed when measuring reagent blanks. In some instances, the contents of the hydrogen peroxide-containing impinger was analyzed for sulfate by the barium thorin method.[6]

Possible interferences resulting from the vaporization and collection of H_2O_2 were studied by passing 28.3 liters of air through 15 ml of 30 percent H_2O_2 solution (cooled to 0°C) and then through three impingers containing acid $CdSO_4$ solution. The latter were then analyzed by the Method II procedure, which was modified as follows: Several drops of 1.0 N ammonium molybdate were added along with the acid-iodine solution to catalyze the reaction of peroxide with iodide ion. Though this reaction goes nearly to completion under the prevailing analytical conditions, the addition of catalyst was made to avoid variations resulting from incompleteness of reaction.

Interferences from substances other than thiols of sulfur dioxide were investigated as follows: Gases were introduced pure or diluted with nitrogen into the sampling train at a flow rate of 1 l/min for 10 minutes, followed by a 15 minute air flush at 1 l/min. Liquid substances were introduced directly into the $CdSO_4$ absorbing solution and analyzed iodimetrically. When a significant analytical difference resulted, an atmosphere of the substance in question was generated by passing nitrogen gas through the liquid at 0°C and estimating gas phase concentrations from the vapor pressure. Approximately 10 liters of the resulting mixture were sampled, followed by a 15 liter air flush. When large quantities of active materials were collected, the recovered absorbing solution was diluted prior to analysis.

SECTION 4

RESULTS AND DISCUSSION

Several reagents were studied as absorption media for H_2S to determine suitability for use in the quantitative collection and separation of H_2S from thiols. Collection efficiencies of H_2S and CH_3SH were measured at various pH values. Figure 2 shows results obtained using zinc acetate/acetic acid solutions. Over the pH range of approximately 5 to 6, the collection efficiency of H_2S is near unity while that of CH_3SH is essentially negligible. However, when $Zn(C_2H_3O_2)_2$ solutions buffered in this pH range were employed for the measurement of gas streams containing mixtures of H_2S and CH_3SH, considerable thiol was collected along with the H_2S, apparently as a result of the coprecipitation of ZnS and mercaptide. These data are shown in Table 1 along with the results of similar measurements made employing alkaline cadmium sulfate (EPA Method 11), buffered cadmium acetate, and cadmium formate solutions. The levels of interference encountered are unacceptably large for any of these reagents to be employed for the collection and separation of H_2S from thiols. Further these results demonstrate that unbuffered zinc acetate (pH 6.0) takes up large quantities of thiols, even when H_2S is absent. Since this reagent is occasionally employed in source sampling tests, potentially large thiol interferences must be expected from its use.

Collection efficiencies of H_2S and CH_3SH in neutral cadmium sulfate solutions were also measured and are shown in Figure 3. Neutral $CdSO_4$ has been previously studied, and the ASTM Method (D2380-68-T) employs 0.57 M $CdSO_4$ to separate H_2S from CH_3SH when concentrations of the latter compound do not exceed 29 mg/m^3. However, in the CH_3SH range employed in the present study (0 - 900 mg/m^3), significant CH_3SH collection was observed at that $CdSO_4$ concentration, even in the absence of H_2S. Therefore, the ASTM Method does not work at these high thiol levels.

A study was also made of $CdSO_4/H_2SO_4$ solutions for the absorption of H_2S from CH_3SH-H_2S feed gas mixtures. Table 1 lists results obtained using 0.16 M $CdSO_4$ at several pH values, which show that thiol interference decreases with decreasing pH and at pH 3.0 does not exceed 4 percent of the H_2S concentration under analysis. The use of 0.16 M $CdSO_4$ was also found to have additional advantages. It is sufficiently concentrated to assure essentially quantitative H_2S collection at pH 3.0 while at the same time providing some buffering against the acidity produced during CdS formation. Sulfate ions have only a weak buffer capacity, but at the concentration and pH employed, it is sufficient to assure that the pH of the absorbing solution is not reduced below the value at which H_2S absorption becomes inefficient, provided that the quantity of H_2S collected does not exceed 0.3 millimoles.

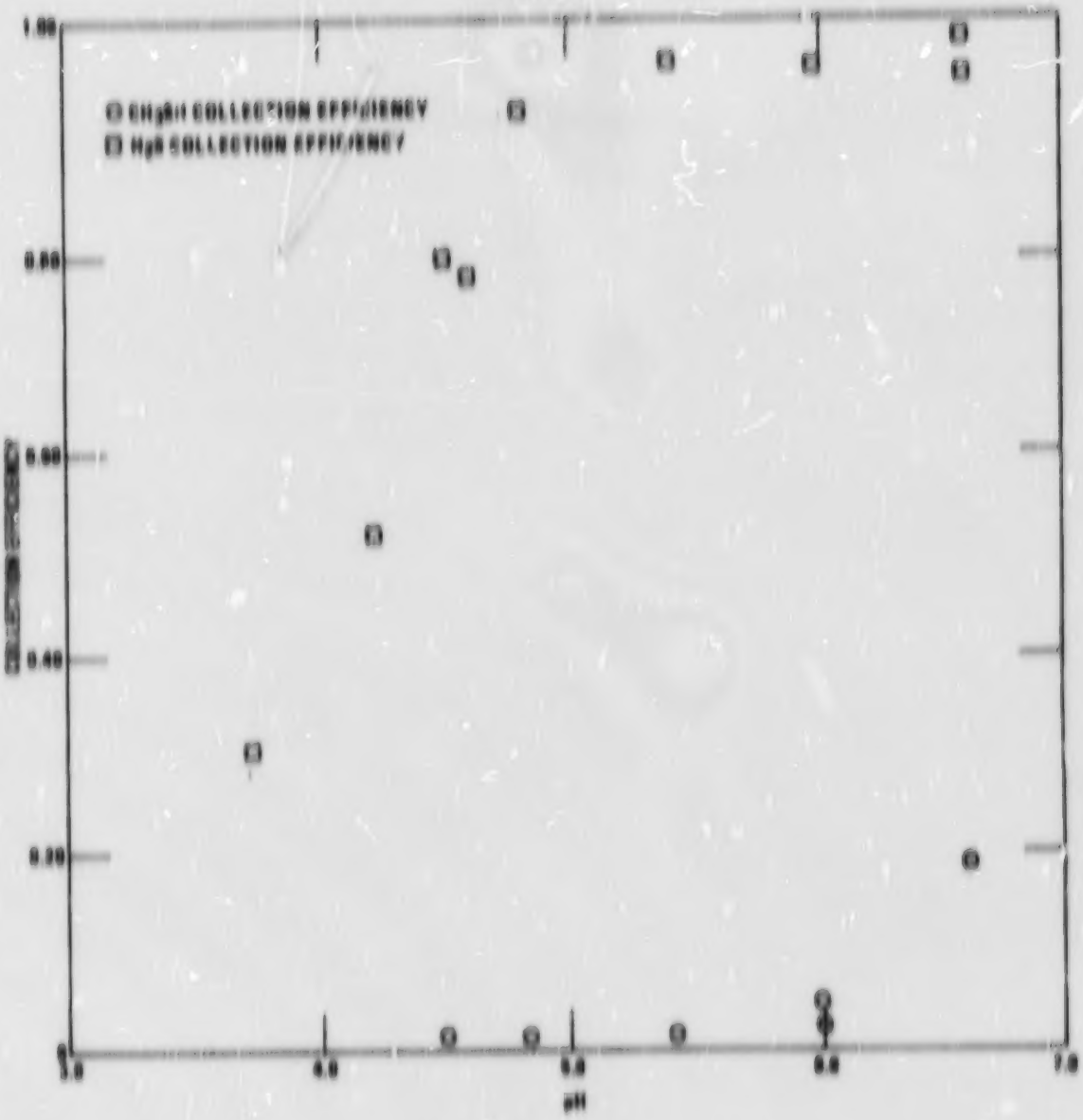

Figure 2. Collection efficiency of Hg0 and CH3Hg in zinc acetate solutions at various pH values.

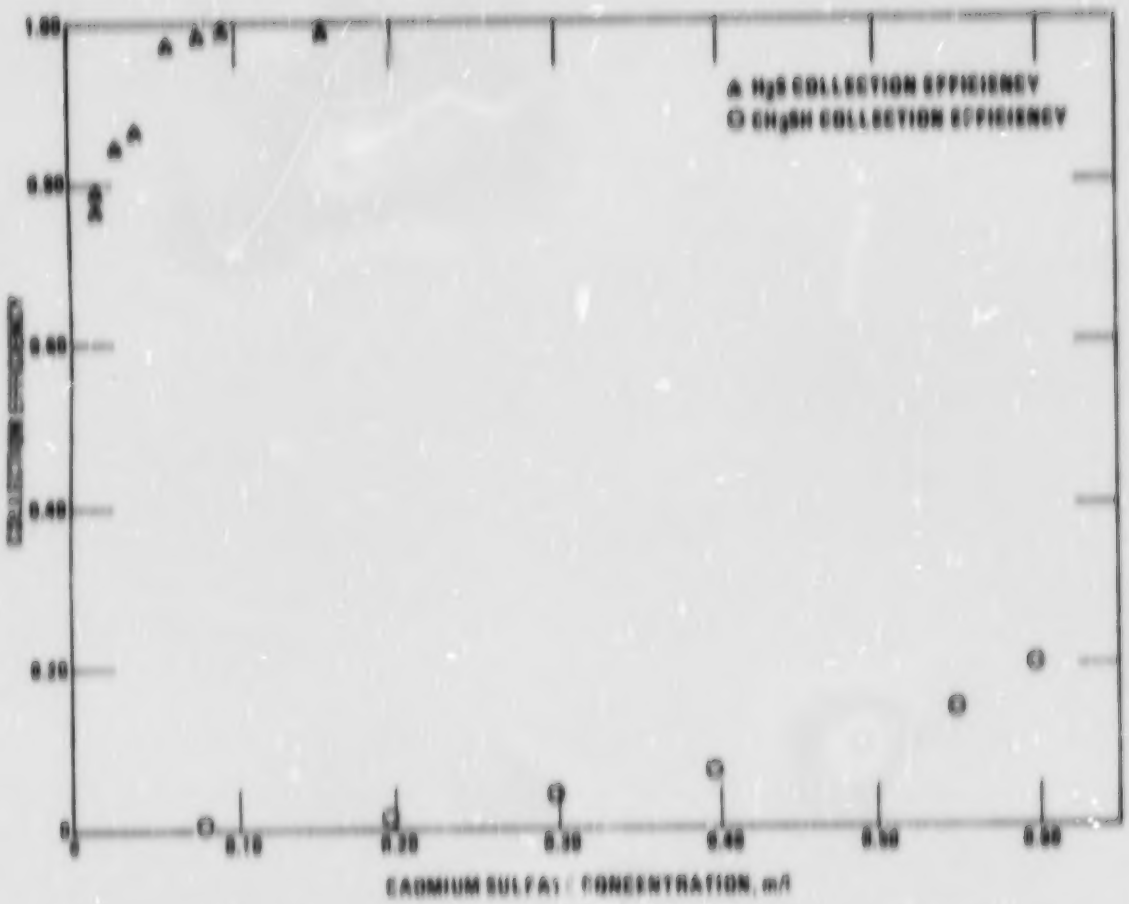

Figure 3. Collection efficiency of H2S and CH3SH in cadmium sulfate solution at various concentrations.

[illegible]

[illegible] at 25°C and 1 atm, and [illegible] at 25°C and 1 atm, [illegible]

[illegible] at 25°C and 1 atm,

The results shown in Table 2 indicate that 3percent H_2O_2 solutions are effective for the removal of SO_2 interferences in H_2S measurements. Values measured after SO_2 removal are statistically equivalent to the concentration of H_2S introduced into the feed gas. (The latter quantity had been determined by substituting an equivalent amount of C_2H_6 diluent gas for the SO_2/C_2H_6 employed.) A small but statistically significant quantity of SO_2 remains after passage through H_2O_2 in gas streams where H_2S is absent. Marked SO_2 interferences result when the peroxide absorbing solution is omitted. In further studies, barium-thorin analysis of H_2O_2 solutions after passage of H_2S-containing feed gases showed that less than 0.2 percent of the quantity of H_2S sampled had been converted to sulfate by the peroxide.

No evidence was found that entrained peroxide is destroyed after it has been collected by acid cadmium sulfate solution. The quantity evaporated from 3 percent peroxide solution was too small to measure accurately, but could be detected. To test for these effects, a more concentrated solution was employed. Entrained peroxide from a 30 percent H_2O_2 solution was collected in acid $CdSO_4$ solution and measured iodimetrically. Results are listed in Table 3 and are compared with a theoretical value. The latter quantity is the quantity of H_2O_2 that would completely saturate a volume equal to the volume of gas passed through the peroxide solution during a typical sampling run (28.3l), at the temperature (0°C) and concentration of interest. This value was determined, employing values of the vapor pressure (0.272 mm) and activity coefficient (0.513) of H_2O_2, calculated from equations given by Scatchard et.al.[9] The measured results are approximately 40 percent of the calculated value; it is therefore possible that complete saturation of the gas stream may not have taken place during the sampling process. However, if the results of these observations are extrapolated, peroxide equivalent to approximately 4 mg H_2S/m^3 must be expected to be entrained by evaporation from the 3 percent H_2O_2 solution employed in Method 11. This quantity is less than 2 percent of the applicable standard and of the same order of magnitude as the reagent blank and standard deviations, examples of which are given in Table 2. However, much larger interferences will result if portions of the hydrogen peroxide solution are transferred into the H_2S collecting impingers, so that caution must be exercised during sampling to avoid this occurrence.

No detectible iodometric measurement resulted from sampling carbon oxysulfide (20 percent in N_2), undiluted ethene, dimethyl sulfoxide, ethanolamine or thiophene. Acetaldehyde and acetone react with iodine and produce unstable titration endpoints. However, the sampling procedure did not result in the complete collection of these compounds in the absorbing solution subjected to analysis. Acetone vapor was largely retained in the peroxide solution while some acetaldehyde was removed by the air flush. Based on the quantities actually measured, acetaldehyde at 2,400 mg/m^3 and acetone at 48,000 mg/m^3 concentrations would be required to produce an interference level equivalent to 10 percent of the applicable H_2S standard. The foregoing compounds were studied as examples of substances that might be found in refinery process gases.

Method II was further investigated by adding measured quantities of sodium sulfide to the absorbing solution. The resulting mixture containing CdS precipitate was then analyzed iodimetrically. These measurements enabled us to study the completeness of sulfide recovery in the analytical part of the method, i.e., in that part that includes processes such as the conversion of CdS to free H_2S, its partial escape into the gas phase, its reabsorption and its subsequent reaction with iodine. It separated out those effects that might have resulted from sampling. Some information about the aging of CdS precipitate also resulted from this investigation. These results are listed in Table 4. The quantities of sulfide employed corresponded to that which would have resulted from feed gases of from 80-280 mg H_2S/m^3. Recoveries differ from 100 percent by amounts that do not exceed 3 percent for all but one determination. The latter corresponded to an H_2S concentration that was only a third of the value of the prominated standard. Table 4 also contains the results of the measurement of samples that were aged for ten days. No appreciable difference between aged and unaged samples could be found. The foregoing served as a check on the compatibility of the absorbing solution with iodimetric measurements and to show the absence of problems resulting from the time interval between sampling and analysis.

TABLE 2. TEST OF REMOVAL OF SO_2 INTERFERENCE BY 3% H_2O_2 SOLUTION

	Feed Gas Composition mg H_2S/m^3		Iodimetrically Active Materials Found, mg H_2S/m^3	
Sample	H_2S	SO_2[b]	H_2O_2 Employed[c]	H_2O_2 Omitted
1	0	176	4.5	178
2	0	176	4.5	174
3	234	176	239	260
4	234	176	243	263
5	234	318	232	340
6	234	318	239	317

[a] Standard deviations of H_2S values in Runs 3-6, SO_2 in Runs 1-4 and SO_2 in Runs 5 and 6 were 5, 2 and 6 mg H_2S/m^3, respectively.

[b] SO_2 concentrations are listed as equivalent mg of H_2S/m^3 at 20°C and 1 Atm., and may be converted to the corresponding mg of SO_2/m^3 values by multiplying by 1.88.

[c] Average Reagent Blank: 12 mg H_2S/m^3; std. dev. 3.

TABLE 3. ENTRAINMENT OF PEROXIDE[a]

Run	Iodometrically Active Materials Detected Micromoles H_2O_2
1	20.6
2	31.0
3	28.9
4	28.4
mean	26.5 ± 4.5[b]
theoretical	66.1

[a] From 30% H_2O_2 solution at 0°C.

[b] Standard Deviation.

[c] Calculated using following constants: volume 28.3 l; vapor pressure, 0.272 mm; mole fraction, 0.3; activity coefficient, 0.513.

TABLE 4. SULFIDE RECOVERY AS PERCENT OF ADDED Na_2S

Na_2S taken millimoles	Sulfide measured millimoles	Percent recovery
0.1865	0.1940	102.9
0.1885	0.1933	102.5
0.0943	0.0954	101.1
0.0566	0.0612	108.1
0.1885	0.1829	97.0
0.1885[a]	0.1829	97.0
0.1885[a]	0.1839	97.6

[a] Samples aged for ten days.

SECTION V

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APPENDIX A

METHOD FOR THE DETERMINATION OF HYDROGEN SULFIDE EMISSIONS FROM PETROLEUM REFINERY FUEL GASES

DISCLAIMER

This method has been assembled from available information based upon extensive laboratory and field evaluations followed by interlaboratory collaborative testing. However, it does not represent an official EPA position at this time.

1.0 Principle and Applicability

1.1 Principle

Hydrogen sulfide (H_2S) is collected from a source in a series of midget impingers and absorbed in pH 3.0 cadmium sulfate solution to form cadmium sulfide (CdS). The latter compound is then measured iodometrically. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering species.

1.2 Applicability

This method is applicable for the determination of hydrogen sulfide emissions from stationary sources only when specified by the test procedures for determining compliance with the new source performance standards.

2.0 Range and Sensitivity

The limit of detection is approximately 5 mg/m^3 (6 ppm). The maximum of the range is 740 mg/m^3 (520 ppm).

3.0 Interferences

Any compound that reduces iodine or oxidizes iodide ion will interfere in this procedure, provided it is collected in the cadmium sulfate impingers. Sulfur dioxide in concentrations of up to 2,600 mg/m^3 is eliminated by the hydrogen peroxide solution. Thiols coprecipitate with hydrogen sulfide. In the absence of H_2S, only traces of thiols are collected. When methane- and ethane-thiols at a total level of 300 mg/m^3 are present in addition to H_2S, the results vary from 2% low at an H_2S concentration of 400 mg/m^3 to 14% high at an H_2S concentration of 100 mg/m^3. Carbon oxysulfide of 20% does not interfere. Certain carbonyl-containing compounds react with iodine and produce recurring end points. However, acetaldehyde and acetone at concentrations of 1 and 3%, respectively, do not interfere.

Entrained hydrogen peroxide produces a negative interference equivalent to 100% of that of an equimolar quantity of hydrogen sulfide. Avoid the ejection of hydrogen peroxide into the cadmium sulfate impingers.

4.0 Precision and Accuracy

Collaborative testing has shown the within-laboratory coefficient of variation to be 3.2% and the overall coefficient of variation to be 5.0%. The method bias was shown to be -4.8% when only H_2S was present.

In the presence of the interferences cited in 3.0 above, the bias was positive at low H_2S concentrations and negative at higher concentrations. At 230 mg H_2S/m^3, the level of the compliance standard, the bias was +2.7%. Thiols had no effect on the precision.

5.0 Apparatus

5.1 Sampling Train

5.1.1 Sampling line - Six to 7 mm (1/4 in.) Teflon* tubing to connect sampling train to sampling valve. Depending on sampling stream pressure, a pressure-reduction regulator may be required just prior to the Teflon sampling line.

If significant amounts of water or amine are present in the sample stream, a corrosion-resistant cold trap should be used immediately after the sample tap. The trap should not be operated below 0°C to avoid condensation of C_3 or C_4 hydrocarbons.

5.1.2 Impingers - Two midget impingers, each with 30 ml capacity. The internal diameter of the impinger tip must be 1.00 mm ± 0.05 mm. The impinger tip must be positioned 4 to 6 mm from the bottom of the impinger.

5.1.3 Glass or Teflon connecting tubing for the impingers.

5.1.4 Ice bath container - To maintain absorbing solution at a low temperature.

5.1.5 Silica gel drying tube - To protect pump and dry gas meter.

5.1.6 Sampling valve - Needle valve or equivalent to adjust gas flow rate. Stainless steel or other corrosion-resistant material.

5.1.7 Dry gas meter - Sufficiently accurate to measure sample volume to within 1% and calibrated with a wet test meter over the range of flow rates used in sampling. Gas volume for one dial revolution must not be more than 10 liters. The gas meter should have a gas petcock or equivalent on the outlet connector which can be closed during the leak test.

5.1.8 Flow meter - Rotameter or equivalent, to measure a 0.5 to 2.0 liters/min (1 to 4 CFH) flow rate.

* Mention of trade names of specific products does not constitute endorsement by the Environmental Protection Agency.

5.1.9 Graduated cylinder - 25 ml size.

5.1.10 Barometer - To measure atmospheric pressure to within ± 2.5 mm (0.1 in.) Hg.

5.1.11 U-Tube manometer - 0-30 cm water column. For leak check procedure.

5.1.12 Rubber squeeze bulb - To pressurize train for leak check.

5.1.13 Tee, pinchclamp, and connecting tubing - For leak check.

5.1.14 Vacuum pump - Required for air purge.

5.1.15 Needle valve or orifice - To set air purge flow to 1 liter/min.

5.1.16 Tube packed with activated carbon - To filter air during purge.

5.1.17 Volumetric flask - One 1,000 ml.

5.1.18 Volumetric pipette - One 15 ml.

5.2 Sample Recovery

5.2.1 Sample container - Iodine flask, glass-stoppered, 500 ml size.

5.2.2 Pipette - 50 ml volumetric type.

5.2.3 Graduated cylinders - One each 25 and 250 ml.

5.2.4 Flasks - 125 ml, Erlenmeyer.

5.2.5 Wash bottle.

5.2.6 Volumetric flasks - Three 1,000 ml.

5.3 Analysis

5.3.1 Flask - 500 ml glass-stoppered iodine flask.

5.3.2 Buretts - 50 ml.

5.3.3 Flask - 125 ml Erlenmeyer

5.3.4 Pipettes, volumetric - One 25 ml; two each 50 and 100 ml.

5.3.5 Volumetric flasks - One 1,000 ml; two 500 ml.

5.3.6 Graduated cylinders - One each 10 and 100 ml.

6.0 Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use best available grade.

6.1 Sampling

6.1.1 Cadmium sulfate absorbing solution - Dissolve 41.0 g of $3CdSO_4 \cdot 8\ H_2O$ and 15.0 ml of 0.1 N sulfuric acid in a 1-liter volumetric flask that contains approximately 3/4 liter of deionized distilled water. Dilute to volume with deionized water. Mix thoroughly. pH should be 3.0 ± 0.1. Add 10 drops of Dow-Corning Antifoam B.* Shake well before use. If Antifoam B is not used, the alternate acidified iodine extraction procedure must be used.

6.1.2 Hydrogen peroxide, 3% - Dilute 30% hydrogen peroxide to 3% as needed. Prepare fresh daily.

6.1.3 Water - Deionized, distilled, to conform to ASTM specifications D1193-72, Type 3.

6.2 Sample Recovery

6.2.1 Hydrochloric acid solution (HCl), 3 N - Add 240 ml of concentrated HCl (specific gravity 1.19) to 500 ml of deionized, distilled water in a 1-liter volumetric flask. Dilute to 1 liter with deionized water. Mix thoroughly.

6.2.2 Iodine solution, 0.1 N - Dissolve 24 g of potassium iodide (KI) in 30 ml of deionized, distilled water. Add 12.7 g of resublimed iodine (I_2) to the potassium iodide solution. Shake the mixture until the iodine is completely dissolved. If possible, let the solution stand overnight in the dark. Slowly dilute the solution to 1 liter with deionized, distilled water, with swirling. Filter the solution if it is cloudy. Store solution in a brown-glass reagent bottle.

* Mention of trade names of specific products does not constitute endorsement by the Environmental Protection Agency.

6.2.3 Standard iodine solution, 0.01 N - Pipette 100.0 ml of the 0.1 N iodine solution into a 1 liter volumetric flask and dilute to volume with deionised, distilled water. Standardise daily as in Section 8.1. This solution must be protected from light. Reagent bottles and flasks must be kept tightly stoppered.

6.3 Analysis

6.3.1 Sodium thiosulfate solution, standard 0.1 N - Dissolve 24.8 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) or 15.8 g of anhydrous sodium thiosulfate ($Na_2S_2O_3$), in 1 liter of deionised, distilled water and add 0.01 g of anhydrous sodium carbonate (Na_2CO_3) and 0.4 ml of chloroform ($CHCl_3$) to stabilise. Mix thoroughly by shaking or by aerating with nitrogen for approximately 15 min and store in a glass-stoppered, reagent bottle. Standardise as in Section 8.2 below.

6.3.2 Sodium thiosulfate solution, standard 0.01 N - Pipette 50.0 ml of the standard 0.1 N thiosulfate solution into a volumetric flask and dilute to 500 ml with distilled water.

6.3.3 Starch indicator solution - Suspend 10 g of soluble starch in 100 ml of deionized, distilled water and add 15 g of potassium hydroxide (KOH) pellets. Stir until dissolved, dilute with 900 ml of deionised distilled water and let stand for 1 hr. Neutralise the alkali with concentrated hydrochloric acid, using an indicator paper similar to Alkacid test ribbon, then add 2 ml of glacial acetic acid as a preservative.
(Note 1: Test starch indicator solution for decomposition by titrating with 0.01 N iodine solution 5 ml of starch solution in 200 ml of distilled water that contains 1 g potassium iodide. If more than 5 drops of the 0.01 N iodine solution are required to obtain the blue color, a fresh solution must be prepared.)

7.0 Procedure

7.1 Sampling

7.1.1 Assemble the sampling train as shown in Figure 1, connecting the five midget impingers in series. Place 15 ml of 3% hydrogen peroxide solution in the first impinger. Leave the second impinger empty. Place 15 ml of the cadmium sulfate absorbing solution in the third, fourth, and fifth impingers. Place the impinger assembly in an ice bath container and place crushed ice around the impingers. Add more ice during the run, if needed.

7.1.2 Connect the rubber bulb and manometer to first impinger, as shown in Figure 1. Close the petcock on the dry gas meter outlet. Pressurize the train to 30-cm water pressure with the bulb and close off tubing connected to rubber bulb. Train must hold a 30-cm water pressure with not more than a 1 cm drop in pressure in a 1-min interval. Stopcock grease is acceptable for sealing ground glass joints.

7.1.3 Purge the connecting line between the sampling valve and the first impinger. Close valve and connect the sample line to the train. Open the petcock on the dry gas meter outlet. Record the initial reading on the dry gas meter.

7.1.4 Open the sampling valve and then adjust the valve to obtain a rate of approximately 1 liter/min. Maintain a constant flow rate during the test. Record the meter temperature.

7.1.5 Sample for at least 10 min. At the end of the sampling time, close the sampling valve and record the final volume and temperature readings.

7.1.6 Disconnect the impinger train from the sampling line. Connect the charcoal tube and the pump, as shown in Figure 1. Purge the train with clean ambient air for 15 min to ensure that all H_2S is removed from the hydrogen peroxide. For sample recovery, cap the open ends and remove to a clean area that is away from sources of heat. The area should be well lighted, but not exposed to direct sunlight.

7.2 Sample Recovery

7.2.1 Discard the contents of the hydrogen peroxide impinger. Carefully rinse the contents of the third, fourth, and fifth impingers into a 500 ml iodine flask.

(Note 2: The impingers normally have only a thin film of cadmium sulfide remaining after a water rinse. If Antifoam B was not used or if significant quantities of yellow cadmium sulfide remain in the impingers, the alternate recovery procedure must be used.)

7.2.2 Pipette exactly 50 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 N HCl to the solution. Quantitately rinse the acidified iodine into the iodine flask. Stopper the flask immediately and shake briefly.

7.2.3 (Alternate) Extract the remaining cadmium sulfide from the third, fourth, and fifth impingers using the acidified iodine solution. Immediately after pouring the acidified iodine into an impinger, stopper it and shake for a few moments, then transfer the liquid to the iodine flask.

Do not transfer any rinse portion from one impinger to another; transfer it directly to the iodine flask. Once the acidified iodine solution has been poured into any glassware containing cadmium sulfide, the container must be tightly stoppered at all times except when adding more solution, and this must be done as quickly and carefully as possible. After adding any acidified iodine solution to the iodine flask, allow a few minutes for absorption of the H_2S before adding any further rinses. Repeat the iodine extraction until all cadmium sulfide is removed from the impingers. Extract that part of the connecting glassware that contains visible cadmium sulfide.

Quantitatively rinse all of the iodine from the impingers, connectors, and the beaker into the iodine flask using deionized, distilled water. Stopper the flask and shake briefly.

7.2.3 Allow to stand about 30 min in the dark for absorption of the H_2S into the iodine, then complete the titration analysis as in Section 7.3.

(Note 3: CAUTION! Iodine evaporates from acidified iodine solutions. Samples to which acidified iodine have been added may not be stored, but must be analysed in the time schedule stated above in 7.2.3.)

7.2.4 Prepare a blank by adding 45 ml of cadmium sulfate absorbing solution to an iodine flask. Pipette exactly 50 ml of 0.01 iodine solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 N HCl. Follow the same impinger extracting and quantitative rinsing procedure carried out in sample analysis. Stopper the flask, shake briefly, let stand 30 min in the dark, and titrate with the samples.

(Note 4: The blank must be handled by exactly the same procedure as that used for the samples.)

7.3 Analysis

(Note 5: Titration analyses should be conducted at the sample-cleanup area in order to prevent loss of iodine from the sample. Titration should never be made in direct sunlight.)

7.3.1 Using 0.01 N sodium thiosulfate solution, rapidly titrate samples in iodine flasks using gentle mixing, until solution is light yellow. Add 4 ml of starch indicator solution and continue titrating slowly until the blue color just disappears. Record V_t, the volume of sodium thiosulfate solution used (ml).

7.3.2 Titrate the blanks in the same manner as the samples. Run blanks each day until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml.

8.0 Calibration and Standards

8.1 Standardize the 0.01 N iodine solution daily as follows: Pipette 25 ml of the iodine solution into a 125-ml Erlenmeyer flask. Add 2 ml of 3 N HCl. Titrate rapidly with standard 0.01 N thiosulfate solution until the solution is light yellow, using gentle mixing. Add four drops of starch indicator solution and continue titrating slowly until the blue color just disappears. Record V_t, the volume of thiosulfate solution used (ml). Repeat until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml and calculate the exact normality of the iodine solution using Equation 9.1. Repeat the standardization daily.

8.2 Standardize the 0.1 N thiosulfate solution as follows: Oven-dry potassium dichromate ($K_2Cr_2O_7$) at 180 to 200°C. Weight to the nearest milligram, 2 g of potassium dichromate into a 500 ml volumetric flask, dissolve in deionized, distilled water and dilute to exactly 500 ml. In a 500 ml iodine flask, dissolve approximately 3 g of potassium iodide (KI) in 45 ml of deionized, distilled water, then add 10 ml of 3 N hydrochloric acid solution. Pipette 50 ml of the dichromate solution into this mixture. Gently swirl the solution once and allow it to stand in the dark for 5 min. Dilute the solution with 100 to 200 ml of deionized distilled water, washing down the sides of the flask with part of the water. Titrate with 0.1 N thiosulfate until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record V_t, the volume of thiosulfate solution used (ml). Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using Equation 9.2. Repeat the standardization each week.

9.0 Calculations

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off results only after the final calculation.

9.1 Normality of the Standard Iodine Solution.

$$N_i = \frac{N_t V_t}{V_i}$$

where N_i = normality of iodine, g-eq/liter;
V_i = volume of iodine used, ml;
N_t = normality of sodium thiosulfate, g-eq/liter; and
V_t = volume of sodium thiosulfate used, ml.

9.2 Normality of the Standard Thiosulfate Solution.

$$N_T = 2.04 \frac{W}{V_T}$$

where W = weight of $K_2Cr_2O_7$ used, g;
V_T = volume of $Na_2S_2O_3$ used, ml;
N_T = normality of standard thiosulfate solution, g-eq/liter; and
2.04 = conversion factor.

$$= \frac{(6 \text{ eq } I_2/\text{mole } K_2Cr_2O_7)\ (1{,}000 \text{ ml/liter})}{(294.2 \text{ g } K_2Cr_2O_7/\text{mole})\ (10 \text{ aliquot factor})}$$

9.3 Dry Gas Volume - Correct the sample volume measured by the dry gas meter to standard conditions (20°C) and 760 mm Hg.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right) \left(\frac{P_{bar}}{P_{std}}\right)$$

where $V_{m_{std}}$ = volume at standard conditions of gas sample through the dry gas meter, standard liters;
V_m = volume of gas sample through the dry gas meter (meter conditions), liters;
T_{std} = absolute temperature at standard conditions, 293 °K;
T_m = average dry gas meter temperature, °K;
P_{bar} = barometric pressure at the orifice meter, mm Hg; and
P_{std} = absolute pressure at standard conditions, 760 mm Hg.

9.4 Concentration of H_2S - Calculate the concentration of H_2S in the gas stream at standard conditions using equation:

$$C_{H_2S} = \frac{K[(V_1N_1 - V_TN_T)\ \text{sample} - (V_1N_1 - V_TN_T)\ \text{blank}]}{V_{m_{std}}}$$

where (metric units):

C_{H_2S} = concentration of H_2S at standard conditions, mg/dscm;
K = conversion factor = 17.0×10^3

$$= \frac{(34.07 \text{ g/mole } H_2S)\ (1{,}000 \text{ liters/m}^3)\ (1{,}000 \text{ mg/g})}{(1{,}000 \text{ ml/liter})\ (2 H_2S \text{ eq/mole})}$$

V_i = volume of standard iodine solution, ml;
N_i = normality of standard iodine solution, g-eq/liter;
V_T = volume of standard sodium thiosulfate solution, ml;
N_T = normality of standard sodium thiosulfate solution, g-eq/liter; and
$V_{m_{std}}$ = dry gas volume at standard conditions, liters.

10.0 Stability

The absorbing solution is stable for at least 1 month. Sample recovery and analysis should begin within 1 hr of sampling to minimize oxidation of the acidified cadmium sulfide. Once iodine has been added to the sample, the remainder of the analysis procedure must be completed according to Sections 7.2.2, 7.2.3, and 7.3.

11.0 References

11.1 "Determination of Hydrogen Sulfide, Ammoniacal Cadmium Chloride Method, API Method 772-54." In: Manual on Disposal of Refinery Wastes, Vol. VI. Sampling and Analysis of Waste Gases and Particulate Matter, American Petroleum Institute, Washington D.C., 1954.

11.2 Tentative Method of Determination of Hydrogen Sulfide and Mercaptan Sulfur in Natural Gas, Natural Gas Processors Association, Tulsa, Oklahoma, NGPA Publication No. 3265-65, 1965.

11.3 Knoll, J. E., M. R. Midgett, "Determination of Hydrogen Sulfide in Refinery Fuel Gases," Environmental Monitoring Series, Office of Research and Development, U.S. EPA, NC 27711.

11.4 Schell, G. W., and M. C. Sharp, "Standardization of Method 11 at a Petroleum Refinery," Midwest Research Institute Draft Report for U.S. EPA, Office of Research and Development, RTP, NC 27711, EPA Contract No. 68-02-1098, August 1976.

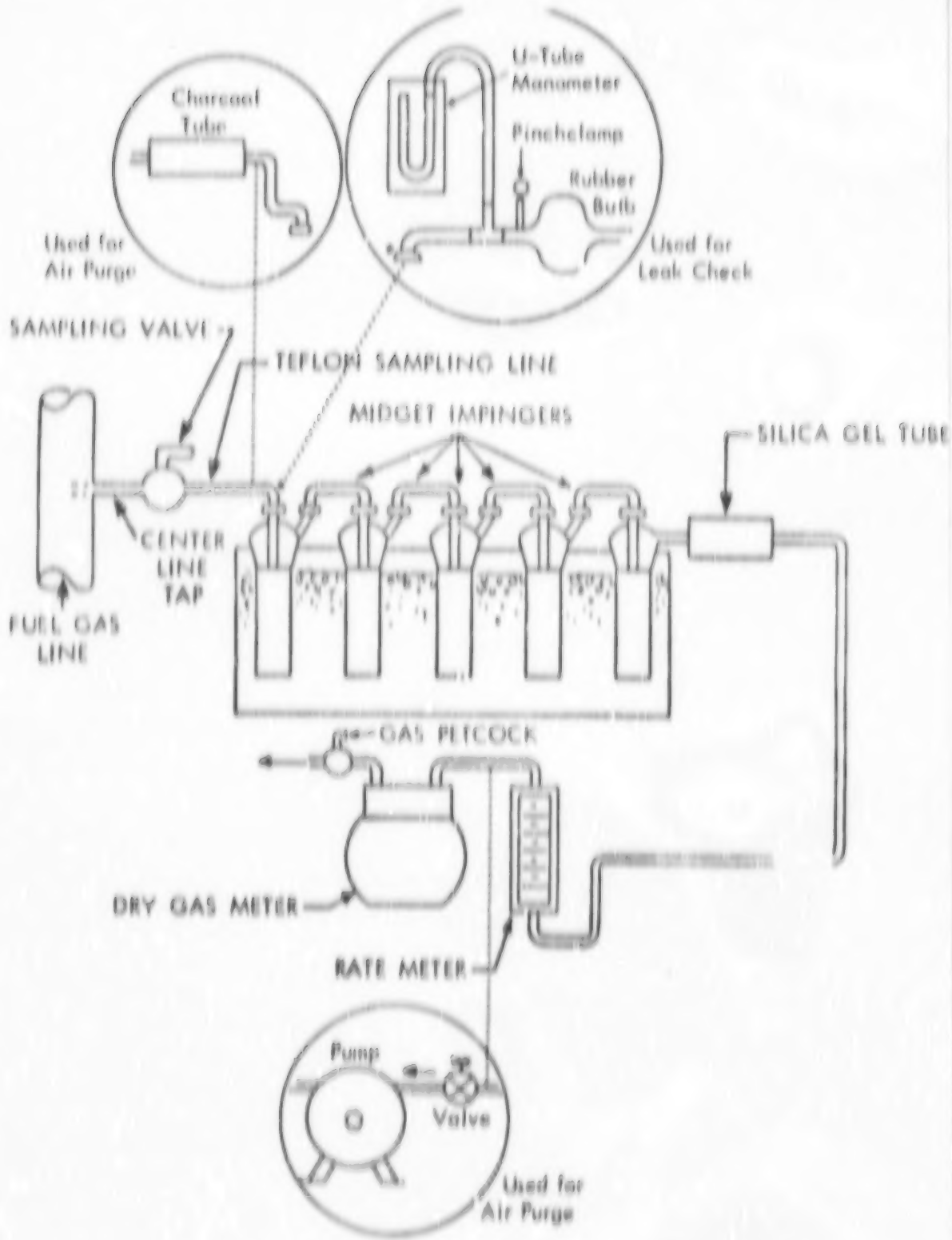

Figure 4 - H_2S Sampling Train

APPENDIX B

CHEMICAL PROCESSES RELEVANT TO METHOD 11

Appendix II. Chemical Processes Relevant to Method II.

The following are the reactions pertinent to the processes discussed in the main body of this report.

Sample analysis:

$$H_2S + CdSO_4 \rightleftharpoons CdS + H_2SO_4 \qquad \text{collection}$$

$$CdS + 2HCl = H_2S + CdCl_2 \qquad \text{acidification}$$

$$H_2S + I_2 = 2HI + S \qquad \text{reaction}$$

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI \qquad \text{measurement}$$

Standardisation:

$$Cr_2O_7^{=} + 14H^{+} + 6I^{-} = 3I_2 + 2Cr^{+++} + 7H_2O$$

$$3I_2 + 6S_2O_3^{=} = 6I^{-} + 3S_4O_6^{=}$$

Sulfur dioxide removal:

$$SO_2 + H_2O_2 = H_2SO_4$$

Interference:

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$$

$$2CH_3SH + I_2 = 2HI + CH_3SSCH_3$$

$$2CH_3SH + 4I_2 + H_2O = CH_3S(O)SCH_3 + 4HI$$

$$2HI + H_2O_2 = I_2 + 2H_2O$$

$$H_2SO_3 + 2H_2S = 3S + 3H_2O$$

$$(CH_3)_2CO + I_2 = CH_3C(O)CH_2I + HI$$

$$(CH_3)_2S + I_2 + H_2O = (CH_3)_2SO + 2HI \qquad \text{slowly}$$

$$O_2 + 4HI = 2I_2 + 2H_2O \qquad \text{slowly}$$